



Dramatically Improve the Safety Performance of Lithium-Ion Battery Separators and Reduce the Manufacturing Cost Using UV Curing and High Precision Coating Technologies

**Dr. John Arnold, PI
June 7, 2017**

Project ID # ES243

Project Overview

Timeline:

Start Date: 10/01/2014

End Date: 6/30/2017

Percent Complete: 99%

Budget:

DOE Share \$1,955,000

Cost share \$ 399,000

FY 15 \$ 376,556

FY 16 \$1,019,444

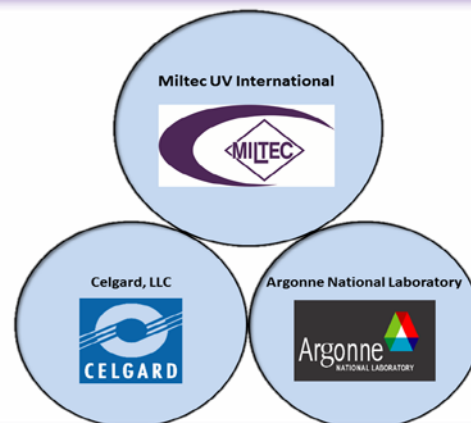
Barriers to Electric Vehicles addressed by this project:

1. **Battery Performance**, improving performance as well as safety
2. **Cost**, reducing costs and improving the quality of ceramic coated separators

Partners

Argonne National Laboratory

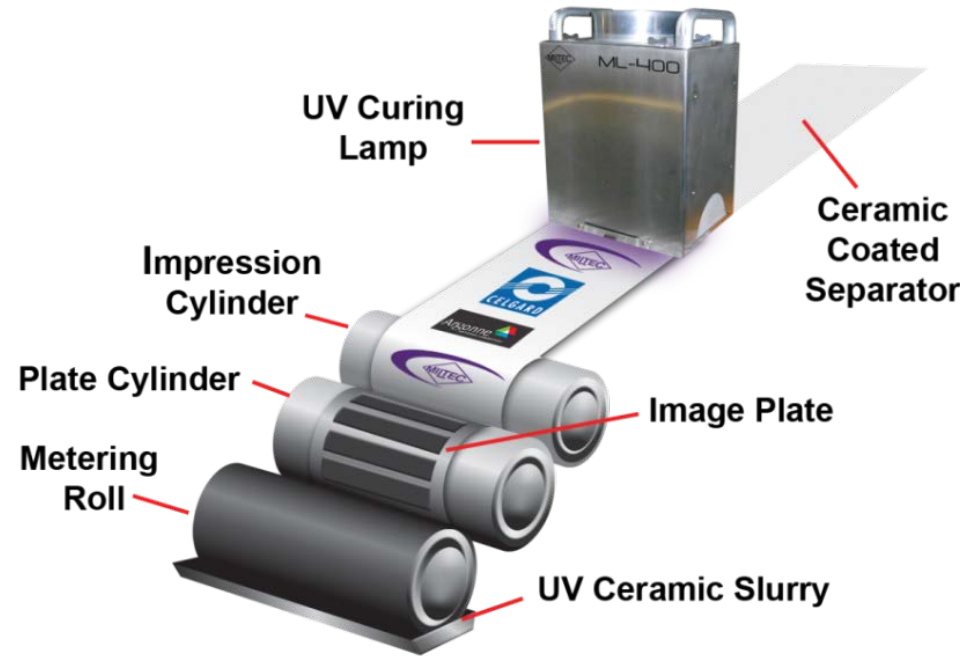
Celgard, LLC



Relevance and Project Objectives

Proposed Project Objectives/Goals:

Improve the shutdown and reduce the risk of thermal runaway and fire, without sacrificing charge and discharge rates, and to reduce the manufacturing ceramic coated separators costs by 50%.



Project's Key Idea/Takeaway:

A revolutionary technology to improve performance and reduce cost of ceramic coated separators.

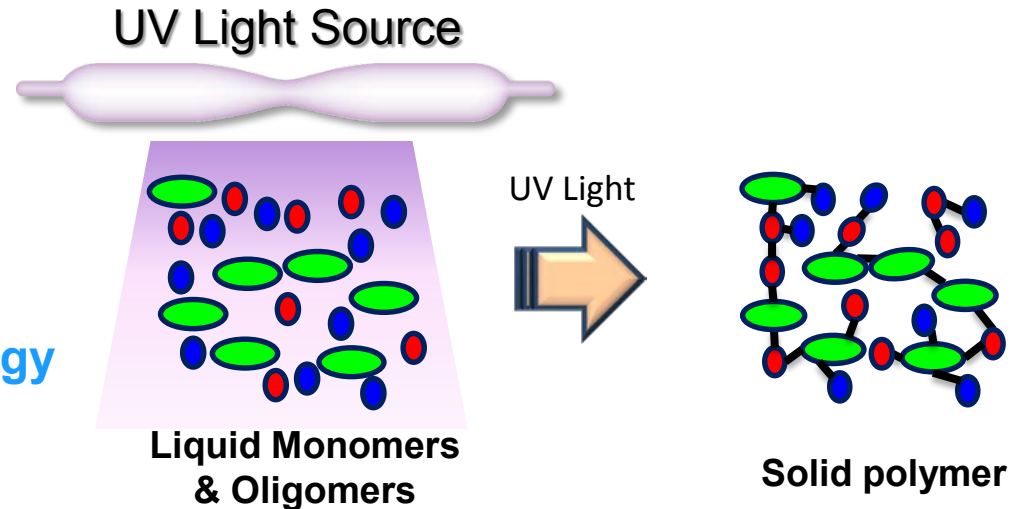
Approach & Milestones	Planned Completion	Status
Budget Period 1		
Project Management Plan	10/16/2014	done
UV curable binder characterization	12/15/2014	done
Adjust UV Curable Binder formulation for printing applications	03/15/2015	done
Printing Pattern Characterization	06/24/2015	done
Separator Coating Laboratory Testing Complete	08/24/2015	done
Complete Separator Electrochemical Evaluation (Go/No-Go)	09/30/2015	done
Budget Period 2		
Complete Initial Printing Press application Validation Tests	12/15/2015	done
Initiate Purchase of Commercial Scale Press	03/18/2016	done
Complete Press Design	06/24/2016	done
Begin Press Shakedown	09/26/2016	done
Complete Final Printing Press Tests	06/26/2017	on target
Complete Cost Model	12/10/2016	done
Complete Cost Reduction Analysis	03/12/2017	done



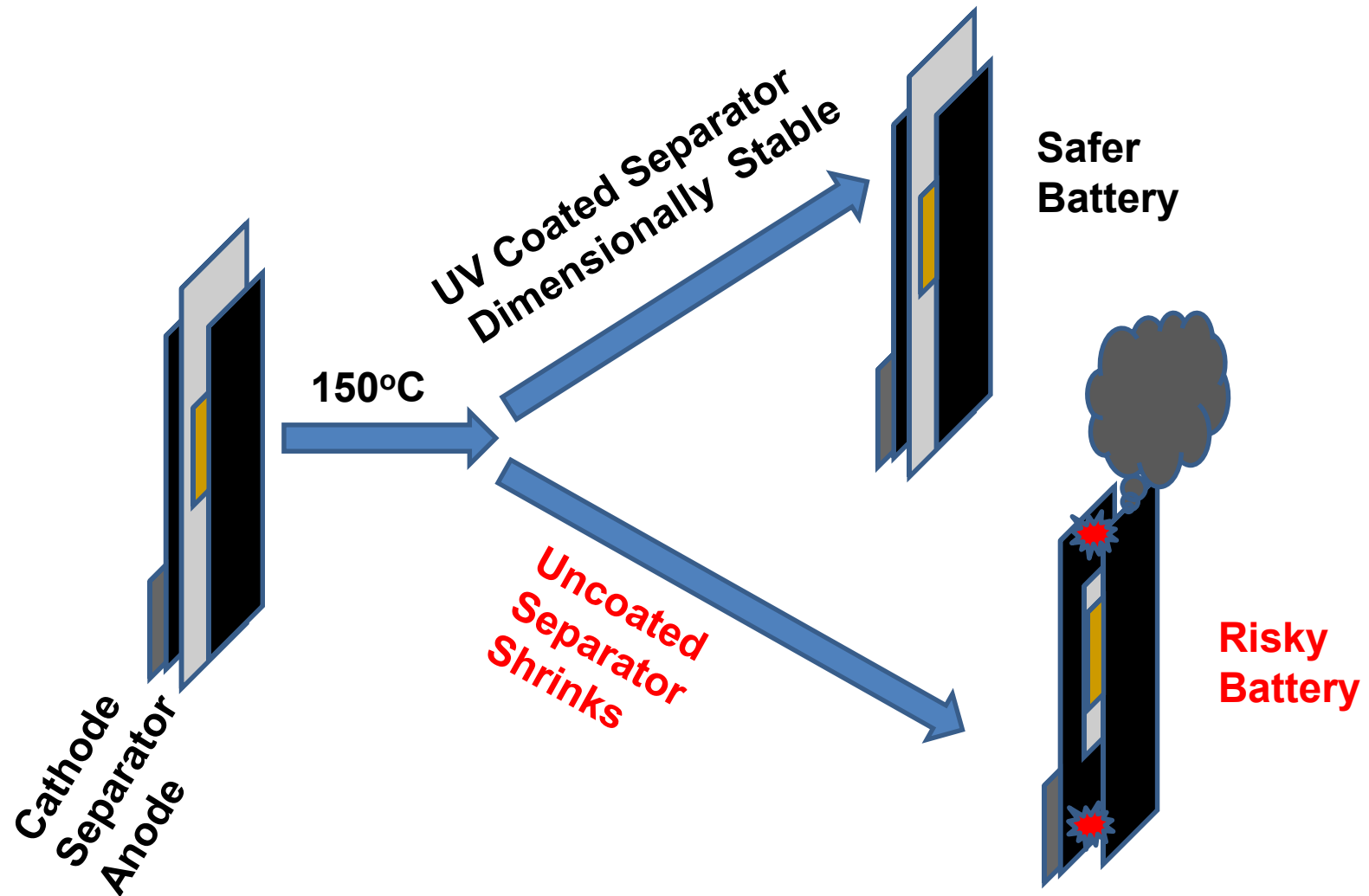
Approach: Reasons to convert to a UV Curable Process

Advantages

- ✓ Oxidation resistance
- ✓ Friendly waterbase technology
- ✓ Fast low temperature drying
122 m/min with UV Lamp
- ✓ Ability to coat any separator film, Trilayer, PE, PP, Polyester
- ✓ A cost model developed shows UV ceramic coating process adds \$0.09-0.25/m² (depending on ceramic price)



Approach: UV Ceramic Coatings Improve Battery Safety



Approach: Why Ceramic Coated Separators and Why UV?

- **General Safety**

- Reduce Dendrite Growth/Penetration
- Improve long term capacity by scavenging cathode and electrolyte decomposition products preventing them from covering anode
- Prevent separator shrinkage during thermal runaway

- **UV Specific**

- Do not appreciably reduce porosity (pattern UV)
- High Voltage Stability (UV crosslinking)
- Significantly less shrinkage
- Easier process to control



Accomplishments 2016

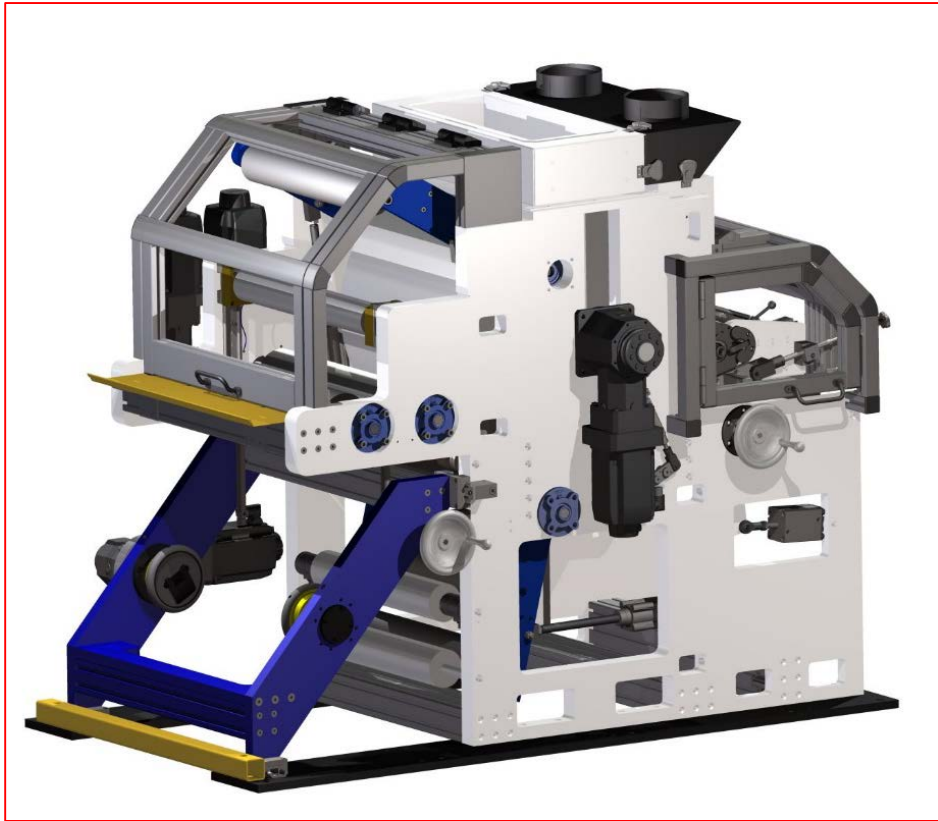
- **Benchtop:** Develop UV binder chemistry with good adhesion; resulting low shrinkage and minimal loss of porosity for ceramic coated separators as means to improve battery safety
- **Lab Press:** Proved printing and coating separator rolls with UV coating works and had the following performance:
 - Developed solid UV coatings for PE, PP, and Trilayer separators with MD shrinkage @ 150°C below 3.0% and often below 1.0% and with Gurley increases $\leq 10\%$ above uncoated separator
 - Tested high voltage stability of UV coating verified in 4.8 V full cell screening test
 - Printed patterned coatings for reduced vehicle weight and higher ion flow, while maintaining shrinkage $<5\%$ at 150°C



Approach 2016-2017

- **Outside Validation:** confirm performance on PP, PE, and trilayer base separator
- **Commercial Scale:** Verified commercial presses exist but are designed for versatile label printing. They use multiple print and coat stations and are not optimized for handling separator film.
- **Develop a Commercial Prototype Press:**

Developed Commercial Prototype Press Printing capable of coating separators at 400 fpm with small footprint



- **Sub-micrometer Coating Thickness Control**
- **Thinner Coatings,**
 - **Less Weight**
 - **More Ion Flow**
 - **Reduced Cost**
- **Patterns for Higher Ion Flow**
- **Versatile: able to Print or Coat**
- **Overcomes unnecessary tension issues compared with commercial multi-station label presses**

Commercial prototype minimizes stress for 400 fpm coating and winding

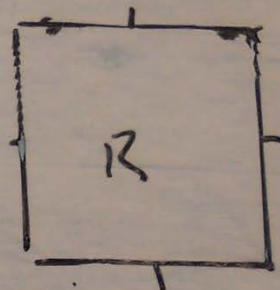
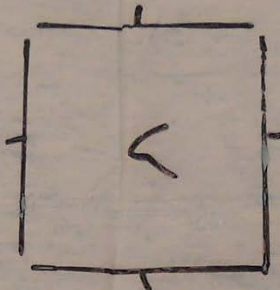
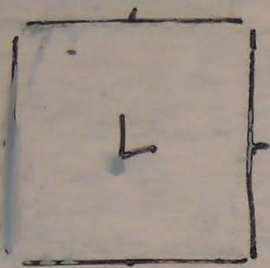


- Designed to reduce tension-stress issues for winding larger separator rolls
- Does not impart stress due to heat or UV curing
- Web fully supported from nip to coating, drying, curing, rewind to eliminate unsupported web stress
- Small footprint also offers maximum manufacturing flexibility.

UV Ceramic Coated 16 μm PE Separator barely shrinks after 0.5 hour @ 180°C.

UV Coated PE
3% MD Shrinkage

← Machine Direction

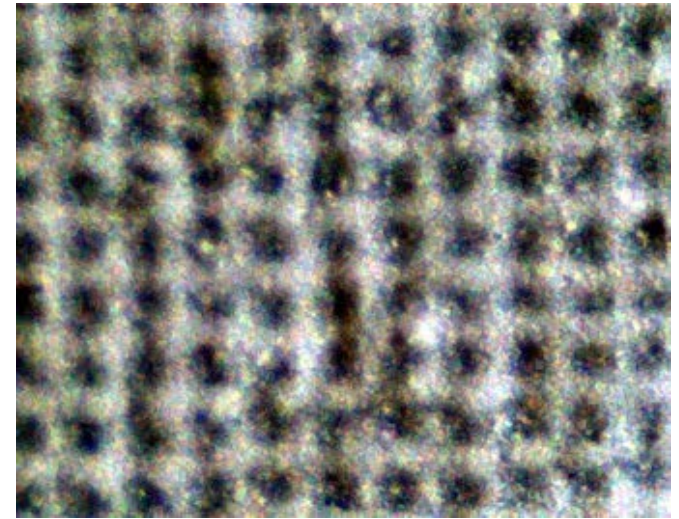


Uncoated PE
65% MD Shrinkage



Advantages of a Printed Ceramic Pattern

1. **More Power from More Ion Flow**
2. **More Energy from Less Weight**
(measured 39% reduction in separator weight for pattern versus a solid coating)
3. **Same Shrinkage as comparable ceramic coating of same thickness**
4. **ANL tests demonstrate the porosity of printed ceramic patterns DOES NOT increase or cause dendrite growth**



Grown Dendrites: do not match Ceramic Pattern on Separator

ANL promoted dendrite growth for 300 cycles w/graphite-lithium metal cell

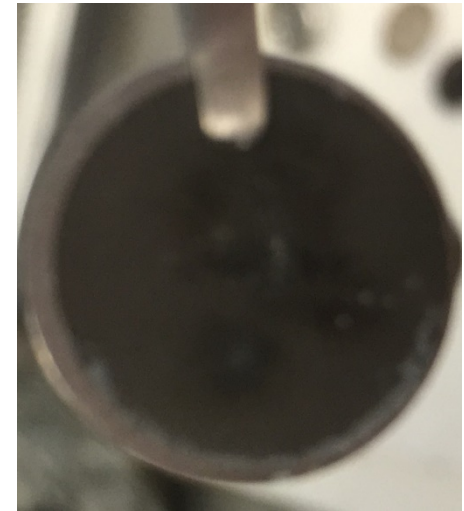
Printed pattern



← 220 μm →
10 x 10 μm



← 20,000 μm →

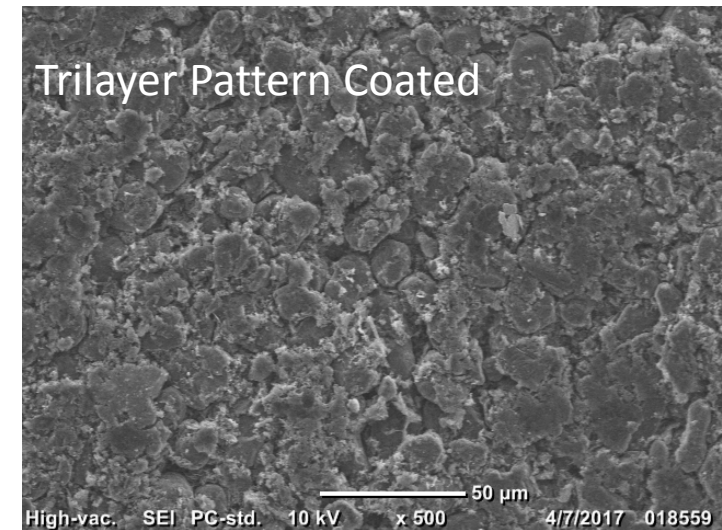
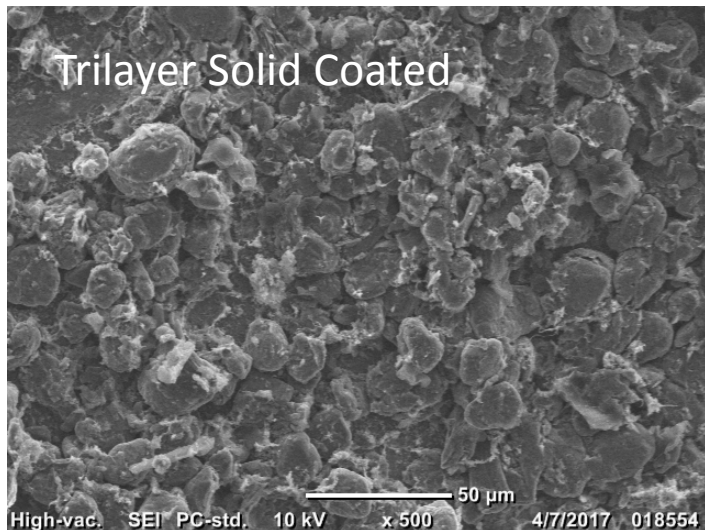
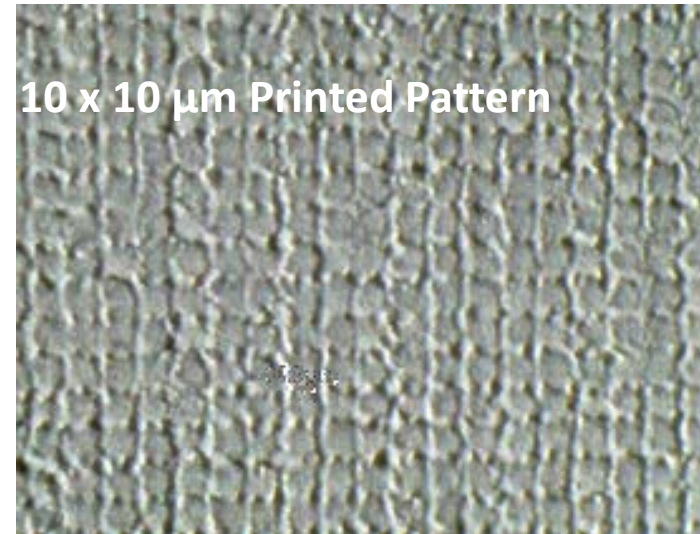
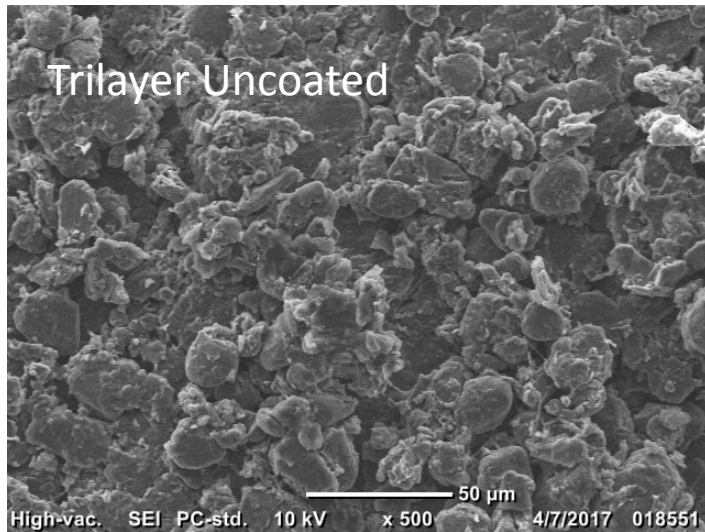


← 18,000 μm →

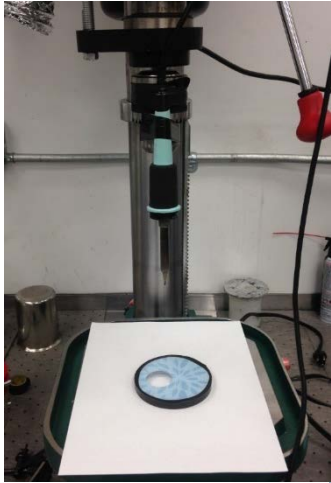
Dendrite did grow on the edge of electrode

—dendrite growth does not match ceramic pattern

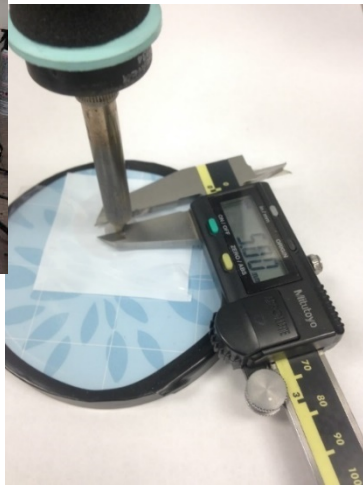
Deep lithiated graphite anodes show no pattern due to solid or patterned UV ceramic coating on separator



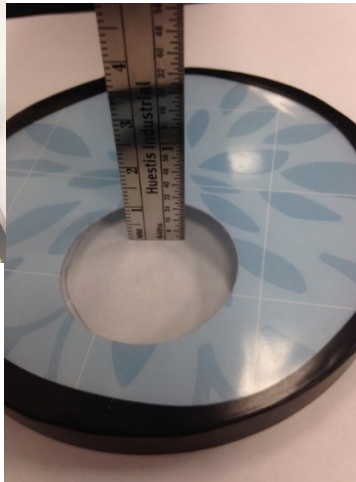
What happens to the separator in a nail penetration test? We simulate this with our hot solder gun penetration test.



335°C solder gun mounted on a drill press



Pushed through separator & held for 5 seconds



At a depth of 10-mm the solder gun is past the tip and the 5-mm wide soldering body touches the separator.

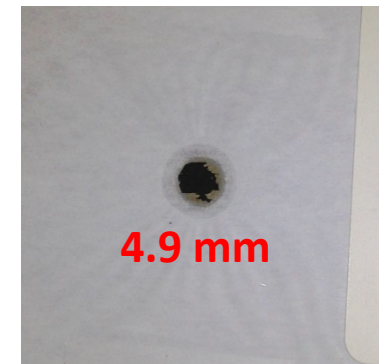
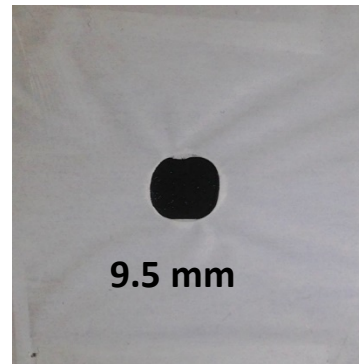
With the right UV ceramic coating we might reduce and slow the ion tidal wave catastrophe in the nail penetration test

Uncoated

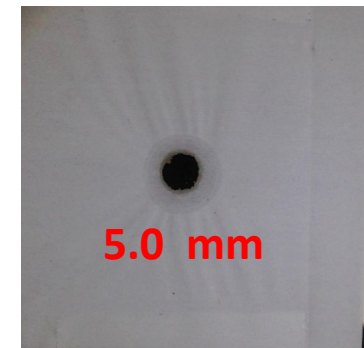
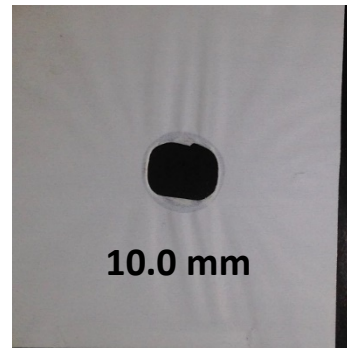
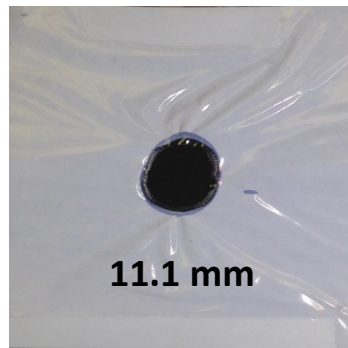
1-side standard UV
Ceramic Coating

Special 2-side
UV Coating

16 μ m PP



16 μ m Trilayer



The special coating prevents the separator from shrinking away from a hot soldering gun



UV Ceramic Coating Process adds \$0.09-\$0.25/m² (range dependent on cost of ceramic)

- **Model Reviewed and Improved by University of Maryland Honors Students (Quest Program)**
- **Cost Model Includes:**
 - **Capital cost (coating-mixing equipment, space, HVAC, etc.)**
 - **Indirect costs (taxes, insurance, interest, fees, etc.)**
 - **Material costs (UV binder, ceramic, waste)**
 - **Operating costs (labor, electricity, consumables, maintenance)**

Accomplishments

- Developed UV coatings for PE, PP, and Trilayer separators with <5% shrinkage at 150°C and Gurley increases $\leq 10\%$ as well. Similar results at 180°C with Trilayer Separator.
- Developed a superior high speed, low temperature, low tension, coating process with a complete commercial prototype UV press
- Confirm ability for high speed coating with uniformity, tension, and consistency.
- Printed patterned coatings for reduced vehicle weight and higher ion flow, while maintaining shrinkage <5% at 150°C and 180°C
- Demonstrated 10- μm patterned coatings do not lead to dentrite growth



Partners



Prepare cells made with Miltec UV ceramic coated separator and evaluate performance

Dr. Khalil Amine, ANL



Conduct tests to confirm adhesion, strength, shrinkage and porosity of Miltec UV ceramic coated samples

Dr. John Zhang, Celgard

Remaining Challenges Future Work

Testing in real battery packs to verify the utility of UV ceramic coatings

- 1. Confirm advantages of special UV ceramic coatings to reduce fire possibility in nail penetration as well as partial shut down features***
- 2. Confirm advantages of printed UV ceramic coating over a solid UV ceramic coating***
- 3. Pouch Cell Data confirming advantages of UV ceramic coatings and alternative lower cost ceramics are in process.**

***Such testing would require new funding**



Summary, 1

- **UV ceramic coatings are capable of achieving all the important properties of a ceramic coated separator:**
 - **0-5% shrinkage at elevated temperatures (150-180°C)**
 - **≤10% increase in Gurley (1-4 µm coatings)**
 - **Excellent adhesion**
 - **Low coating weight and**
 - **High speed processing +200 fpm.**
- **UV process leads to short web path, less unsupported web, which leads to better yields and less scrap.**

Summary, 2

- **Miltec's UV process has less stress and ability to send customers larger rolls with constant inner outer stress, which reduces the battery manufactures labor & down time as well.**
- **UV ceramic coatings are crosslinked, which benefits high voltage and chemical resistance for future batteries.**
- **UV with printing technologies may lead to faster charge/discharge & lesser weight than other ceramic coated separators, without sacrificing battery safety.**